DIAMOND-FILM LUBRICANTS FOR CERAMICS

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Introduction

Diamond's excellent tribological properties make it an ideal material for many tribological applications. Its extreme hardness, high abrasion resistance, good fatigue strength, high thermal conductivity, good radiation and temperature resistance, chemical and thermal inertness, high corrosion resistance, and environmental compatibility (refs. 1 and 2) suit it for applications such as bearings, valves, and engine parts in the harsh environment found in internal-combustion and jet engines. For example, diamond is being considered as a replacement for the sapphire that slides against tungsten carbide poppets which are used in check valves for the Space Shuttle's forward reaction control subsystem and orbital maneuvering subsystem.

Both natural and high-pressure synthetic diamond have limited application because of the small size and the high cost of the crystals. Another limiting factor for tribological applications is the separate operation that is required to bond the crystals to a substrate. Chemical-vapor-deposited (CVD) diamond, on the other hand, offers a broader potential since size and, eventually, cost are less of a limitation. CVD diamond, which is available in planar film or sheet form, opens the door for design engineering and tribology to take full advantage of the intrinsic properties of diamond in such areas as wear, solid lubrication, erosion, and corrosion applications.

The major drawbacks of CVD diamond, which restrict its use as a tribological coating, are its very rough surface, its low bending strength, and its very high deposition temperature. These obstacles must be overcome before practical, reliable, and cost-effective diamond coatings will become available as wear-resistant self-lubricating barriers for many moving mechanical assemblies. A process must be developed that will keep the deposition temperature below 400 °C and provide consistently satisfactory adhesion to metallic and nonmetallic substrates, including steel and Si_3N_4.

Experimental

Sliding friction experiments were conducted with CVD diamond films and diamondlike carbon (DLC) films in contact with natural diamond or with a polished CVD diamond pin in humid air, in dry nitrogen, and in ultrahigh vacuum. The diamond films were produced by microwave plasma CVD and hot-filament CVD techniques. The DLC films were produced by an ion-beam deposition technique. Various analytical techniques, including Raman spectroscopy, hydrogen forward scattering (proton recoil analysis), Rutherford backscattering, transmission and scanning electron microscopy, X-ray photoelectron spectroscopy, and X-ray diffraction, were utilized to characterize the films.

CVD Diamond Films

In humid air and dry nitrogen, as-deposited fine-grain diamond films and polished coarse-grain diamond films both had a low coefficient of friction (<0.1) and a low wear rate ($\leq 10^{-6}$ mm^3/N·m). In ultrahigh vacuum, however, they had a high coefficient of friction (>0.4) and a high wear rate ($\geq 10^{-4}$ mm^3/N·m), making them unacceptable for tribological applications. Thus, it is clear that surface modifications which provide acceptable levels of friction and wear properties, regardless of environment, will be necessary before diamond films can be widely used for tribological applications.

Ion-Implanted Diamond Films

Bombarding diamond films with carbon ions at 60 keV or nitrogen ions at 35 keV produced a thin, superficial layer of amorphous nondiamond carbon (<0.1 μm thick). The carbon- or nitrogen-ion implantation had little effect on the coefficient of friction in humid air or in dry nitrogen: The ion-implanted diamond film retained a low coefficient of friction (≤0.1) and a low wear rate (≤ 10^{-6} $mm^3/N{\cdot}m$). In this respect, the ion-implanted CVD diamond was similar to the as-deposited fine-grain or the polished coarse-grain CVD diamond. In ultrahigh vacuum, however, the effect of carbon- or nitrogen-ion implantation was significant: An amorphous nondiamond carbon layer was formed on the diamond films, thereby reducing the coefficient of friction to 0.1 or lower and the wear rate to 10^{-6} $mm^3/N{\cdot}m$, making them acceptable for tribological applications. The much lower friction of the ion-implanted diamond films can be attributed to the combination of the low shear strength of the thin, amorphous nondiamond carbon surface layer and the small contact area resulting from the high elastic modulus and hardness of the underlying diamond film.

We know that ion implantation does not create an interface of demarcation between the host material and the implanted species. Instead, it produces a graded interface. The ion implantation process can be easily controlled by adjusting the operating variables of the accelerator, such as the accelerating energy, current density, and time. One disadvantage of ion implantation technology is that the depth of penetration of the implanted species is very shallow (the thickness of ion-implanted layers ranges from 0.01 to 0.5 μm) compared with that of conventional coatings; this may limit the tribological applications of ion-implanted coatings to light loads or short-term operations. In other words, the endurance life (wear life) of the ion-implanted layer that contributes to the tribological benefits is limited.

Diamondlike Carbon Films on CVD Diamond

The thickness of (DLC) films can range from 0.1 to 5 μm, which is an order of magnitude greater than that of the ion-implanted layer. As a result, the endurance life of DLC can be longer than that of the ion-implanted layer. For this reason, studying an amorphous DLC film coated on a fine-grain CVD diamond film was a logical approach to enhancing tribological properties—especially, increasing the endurance of CVD diamond films.

As part of this study, DLC films were produced on fine-grain CVD diamond coatings by the direct impact of an ion beam (composed of a 3:17 mixture of Ar and CH_4) at ion energies of 1500 and 700 eV. In ultrahigh vacuum the ion-beam-deposited DLC films on fine-grain CVD diamond (like the ion-implanted CVD diamond) greatly decrease both the friction and wear of fine-grain CVD diamond films and provide solid lubrication. In dry nitrogen and in humid air, the ion-beam-deposited DLC films on fine-grain CVD diamond films also had a low steady-state coefficient of friction and a low wear rate. Such enhanced tribological performance, coupled with a wider range of coating thicknesses, means a longer endurance life and improved wear resistance for the DLC deposited on fine-grain CVD diamond in comparison to the ion-implanted diamond films. Thus, DLC deposited on fine-grain CVD diamond films can be an effective wear-resistant, lubricating coating regardless of environment.

In this investigation the main criteria for judging the performance of a potential diamond-film lubricant were the coefficient of friction and the wear rate, which had to be less than 0.1 and 10^{-6} $mm^3/N{\cdot}m$, respectively. The following films met the requirements regardless of environment:

- Carbon- or nitrogen-ion-implanted, fine-grain CVD diamond
- DLC deposited on fine-grain CVD diamond

References

1. Pierson, H.O.: Handbook of Carbon, Graphite, Diamond, and Fullerenes. Properties, Processing, and Applications. Noyes Publications: Park Ridge, NJ, 1993.

2. Davies, G., ed.: Properties and Growth of Diamond. Inspec., Institution of Electrical Engineers, London, UK, 1994.

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Some earlier data and experimental details on this research are given in the following:

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- Miyoshi, K., et. al.: Friction and Wear of Plasma-Deposited Diamond Films. J. Appl. Phys., vol. 74, no. 7, Oct. 1993, pp. 4446-4454.

- Wu, R.L.C., et. al.: Ion-Implanted Diamond Films and Their Tribological Properties. Sur. Coat. Technol., vol. 62, 1993, pp. 589-594.

- Miyoshi, K., et al.: Physical and Tribological Characteristics of Ion-Implanted Diamond Films. NASA TM-106682, 1994.

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  - performing Rutherford backscattering spectroscopy, hydrogen forward scattering, x-ray diffraction, and Raman analysis

- P.J. Wilbur and B. Shogrin of the Colorado State University for carbon ion implantation

- M. Murakawa and S. Miyake of the Nippon Institute of Technology for
  - hot-filament CVD diamond film deposition
  - nitrogen ion implantation

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Fig. 1

Sapphire and Diamond Sliding Against Tungsten Carbide Poppet

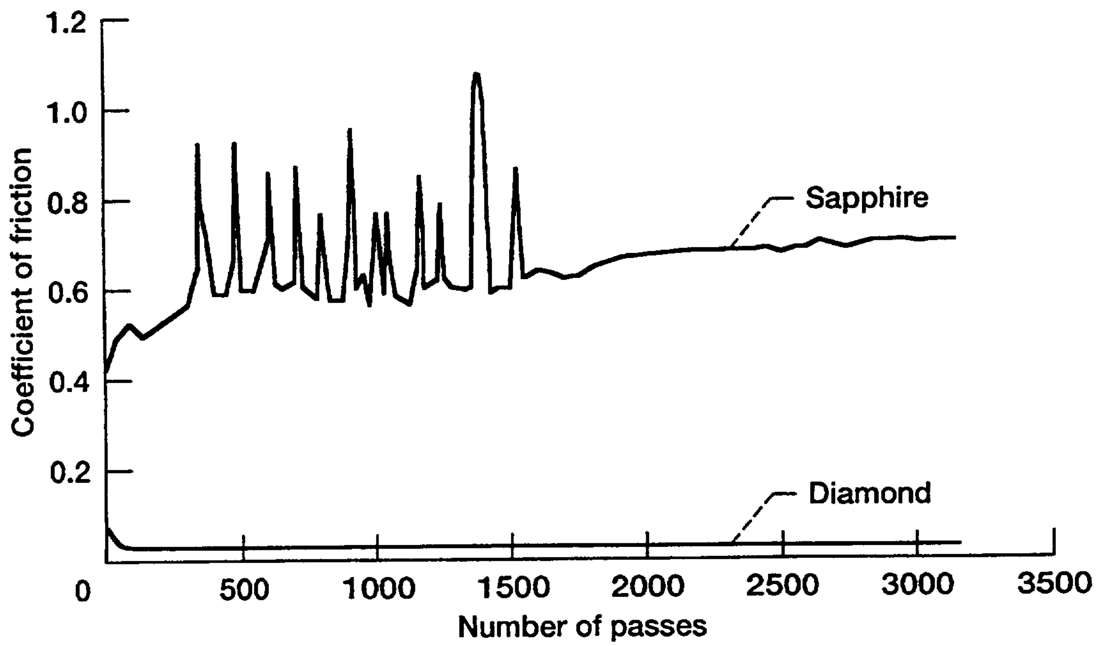

Fig. 2

Why Diamond?

Tribological Advantages

- Extreme hardness
- High abrasion resistance
- Good fatigue strength
- High thermal conductivity
- Good radiation and temperature resistance
- Chemical and thermal inertness
- High erosion and corrosion resistance
- Environmental compatibility

Aeropropulsion and Rocket Propulsion Applications

- Self-lubricating, wear resistant barriers for moving mechanical assemblies such as bearings, valves, and engine parts
- Film lubricants for ceramics such as Si_3N_4, SiC, Al_2O_3, . . .
- Hard-to-machine applications for metals, ceramics, and composites

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Fig. 3

Hardness of Diamond and Other Hard Materials

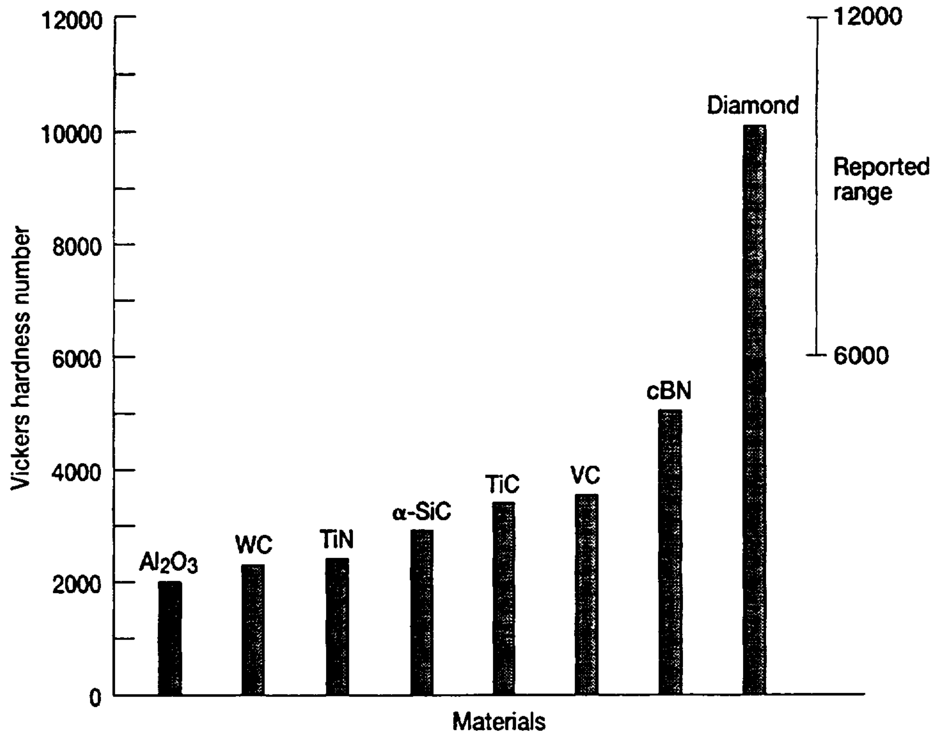

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Fig. 4

Advantages of CVD Diamond

- Planar film or sheet
- Large area
- Properties of diamond

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Fig. 5

Objective

- To provide diamond films with acceptable levels of friction and wear properties regardless of environment

Goals

- Coefficient of friction ≤ 0.1
- Wear rate $\leq 10^{-6}$ mm^3/N•m

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Fig. 6

Analytical Techniques

- Scanning and transmission electron microscopy (SEM and TEM)
  — to determine surface morphology and grain size
- Rutherford backscattering spectroscopy (RBS)
  — to identify impurities and
  — to determine carbon and impurity concentrations
- Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR)
  — to characterize diamond quality and structure
- Hydrogen forward scattering (Proton recoil detection)
  — to measure the hydrogen concentration
- X-ray photoelectron spectroscopy (XPS)
  — to characterize surface chemistry
- X-ray diffraction
  — to determine the crystal orientation

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Fig. 7

Chamber Tribometer

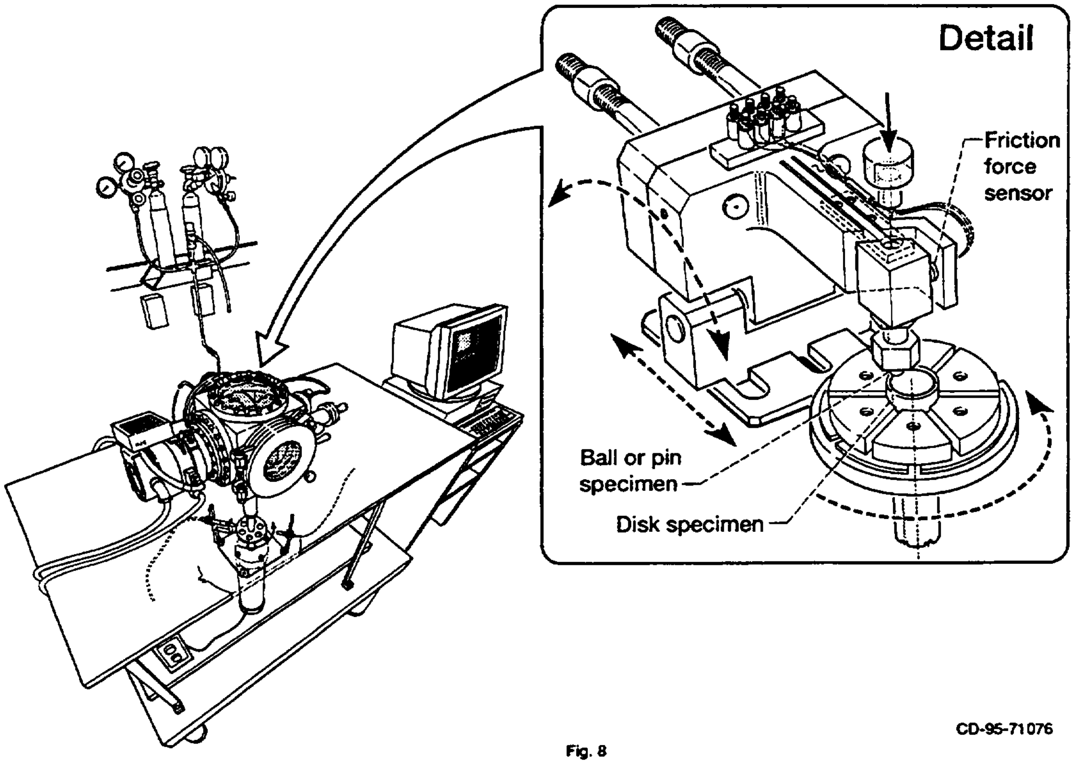

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Fig. 8

Tribological Characterization

- Humid air (40% relative humidity)
- Dry nitrogen (< 1% relative humidity)
- Ultrahigh vacuum (10^{-7} Pa)

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Fig. 9

Fine-grain Diamond and Diamondlike Carbon Films

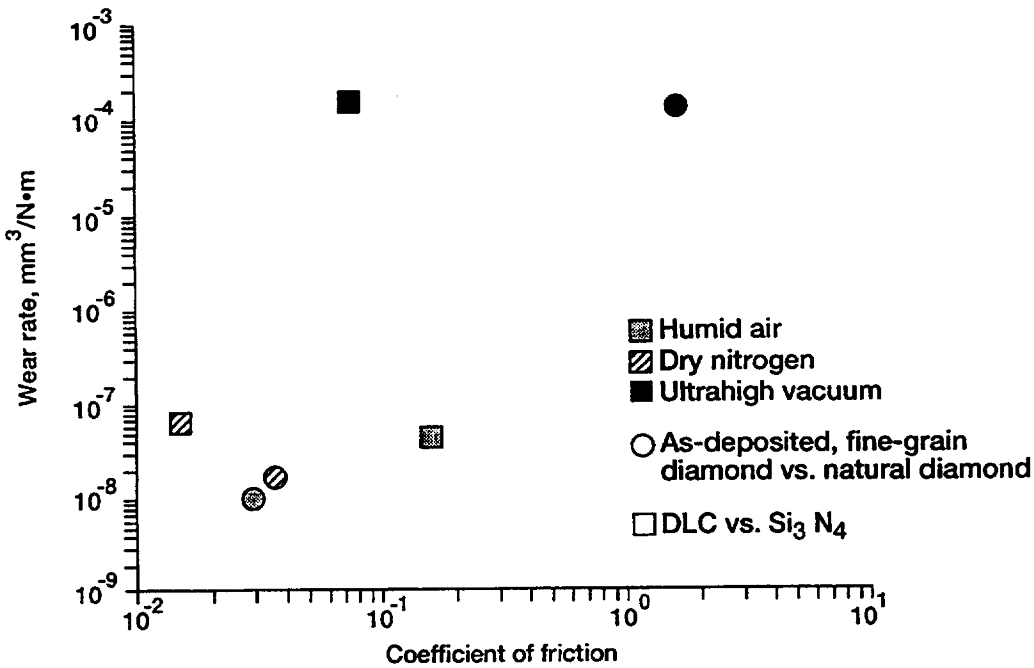

Fig. 10

High Adhesion, Friction, and Wear in Ultrahigh Vacuum

- Removing some contaminant surface layer from the contact area yielded stronger interfacial adhesion, friction, and wear
    - Coefficient of friction > 1
    - Wear rate 10^{-4} mm^3/N•m

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Fig. 11

Approach

To use fine-grain diamond and DLC films regardless of environment, we must modify films (e.g., by ion implantation) to obtain acceptable levels of friction and wear properties

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Fig. 12

Types of Diamond Films

- As-deposited, smooth surface of fine-grain CVD diamond
  Microwave-plasma-assisted CVD technique
- Polished, smooth surface of coarse-grain CVD diamond
  Hot-filament CVD technique
- Carbon-ion-implanted surface of fine-grain CVD diamond
  60 keV and 50 $\mu A/cm^2$, 1.2×10^{17} carbon ions/cm^2
- Nitrogen-ion-implanted surface of coarse-grain CVD diamond
  35 keV, 5×10^{17} nitrogen ions/cm^2

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Fig. 13

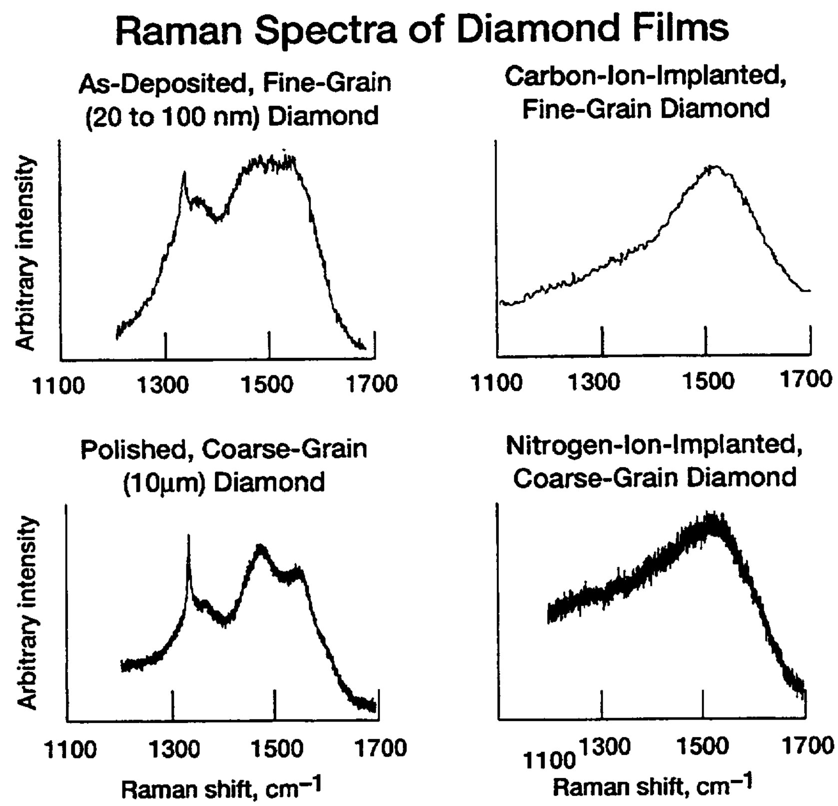
Raman Spectra of Diamond Films
As-Deposited, Fine-Grain (20 to 100 nm) Diamond
Carbon-Ion-Implanted, Fine-Grain Diamond
Polished, Coarse-Grain (10μm) Diamond
Nitrogen-Ion-Implanted, Coarse-Grain Diamond
Arbitrary intensity
1100
1300
1500
1700
Raman shift, cm⁻¹
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Fig. 14

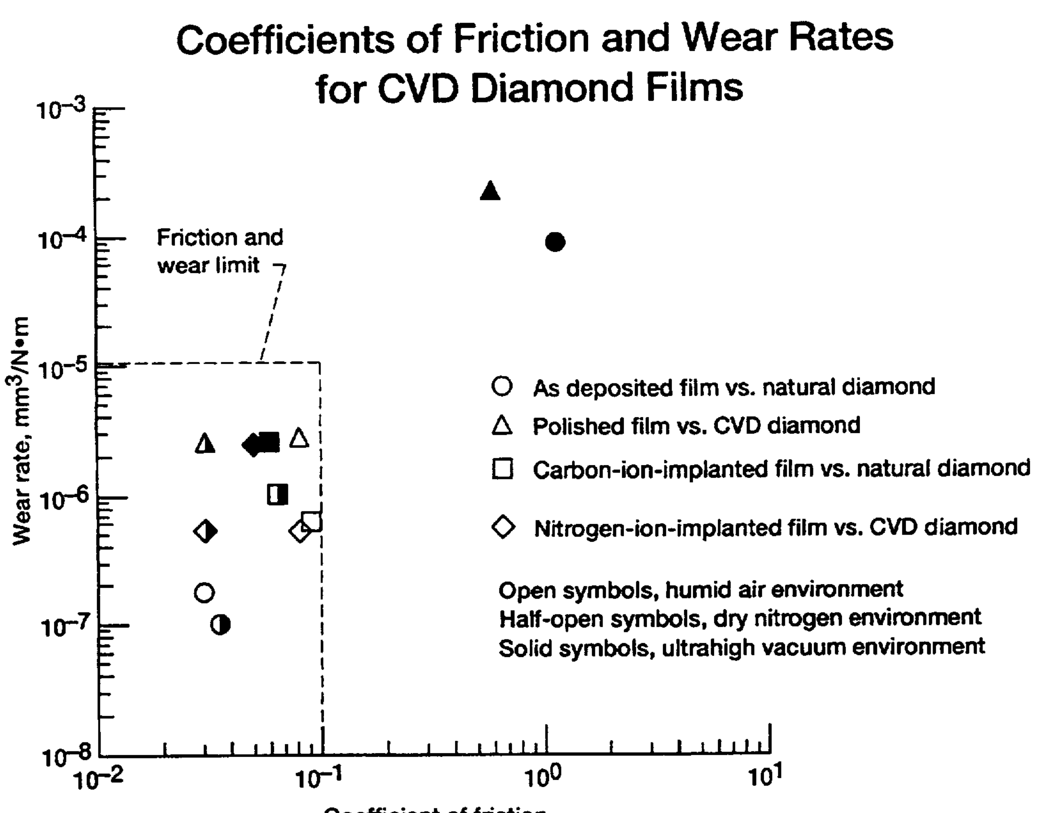
Coefficients of Friction and Wear Rates for CVD Diamond Films
Wear rate, mm³/N•m
10⁻³
10⁻⁴
10⁻⁵
10⁻⁶
10⁻⁷
10⁻⁸
Friction and wear limit
As deposited film vs. natural diamond
Polished film vs. CVD diamond
Carbon-ion-implanted film vs. natural diamond
Nitrogen-ion-implanted film vs. CVD diamond
Open symbols, humid air environment
Half-open symbols, dry nitrogen environment
Solid symbols, ultrahigh vacuum environment
10⁻²
10⁻¹
10⁰
10¹
Coefficient of friction
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Fig. 15

Ion-Implanted Diamond Film

- Ion implantation had a substantial effect on friction and wear
  - Coefficient of friction ≤ 0.1
  - Reduced friction by factors of 10 to 30
  - Wear rate 10^{-6} $mm^3/N \cdot m$
  - Reduced wear by factors of 30 to 90

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Fig. 16

Raman Spectra

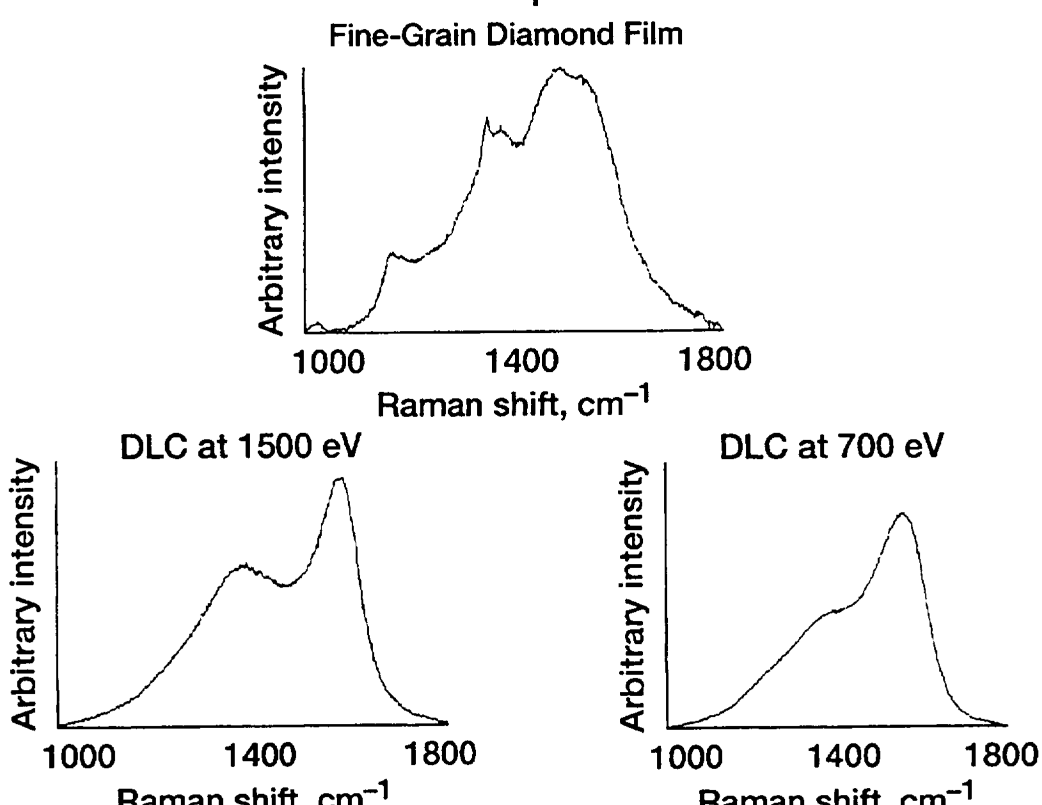

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Fig. 17

Coefficients of Friction and Wear Rates

In Sliding Contact With CVD Diamond Pins in UHV

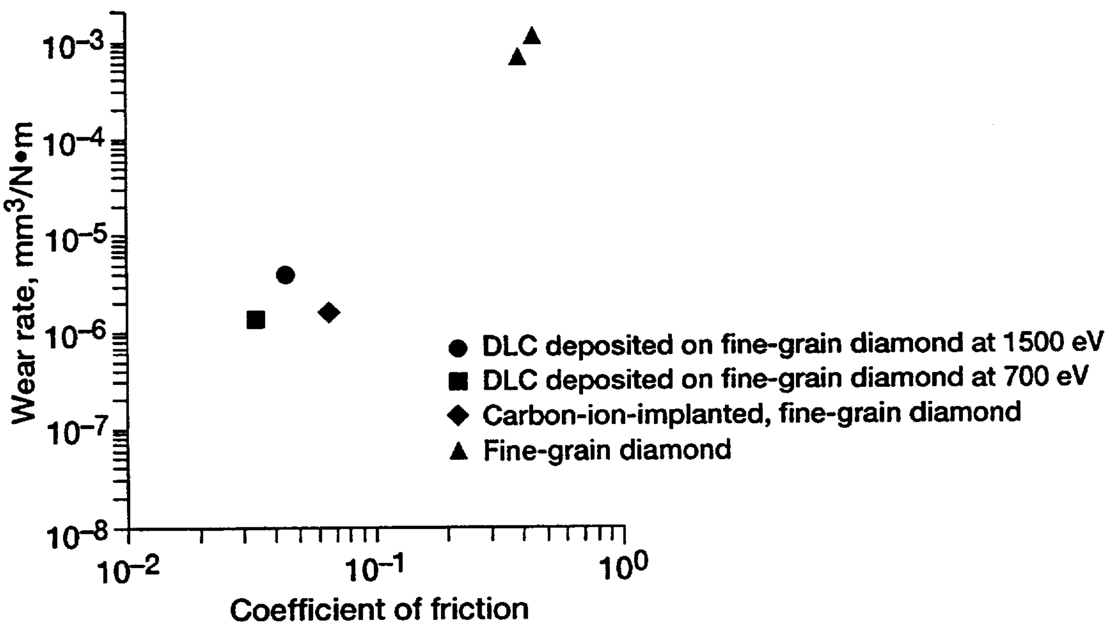

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Fig. 18

Summary

The DLC film produced by direct ion-beam deposition at ion energies of 1500 and 700 eV greatly decreased both the friction and wear of fine-grain CVD diamond films in ultrahigh vacuum without sacrificing the low friction and low wear properties attainable in dry nitrogen and in humid air.

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Fig. 19

Mechanisms of Friction

$\mu \propto \gamma A$
or
$\mu = \frac{sA}{W}$

γ Surface energy (bonding energy)
s Shear strength of junctions
A Real area of contact
W Load

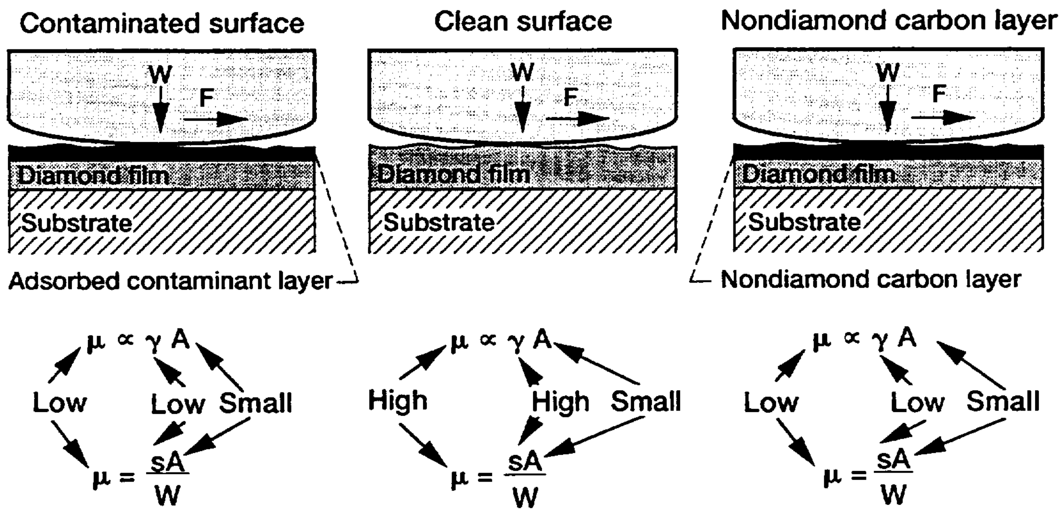

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Fig. 20

Concluding Remarks

The main criteria for judging the performance of a potential diamond-film lubricant were the coefficient of friction and the wear rate, which had to be less than 0.1 and 10^{-6} $mm^3/N{\cdot}m$, respectively.

The following films met the requirements regardless of environment:

- Carbon- or nitrogen-ion-implanted, fine-grain diamond
- DLC deposited on fine-grain diamond

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Fig. 21

Future Work

- Complete tribological evaluation of CVD diamond-film lubricants and related multilayer coatings at temperatures up to 600 °C
- Determine optimum multilayer thin film materials for antiwear/antifretting applications

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Fig. 22